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(54) **Process for producing inorganic particulate material in the form of fine balls approximately uniform in size**

Verfahren zur Herstellung von feinkugeligen, gleichförmig grossen anorganischen Teilchen

Procédé de production des particules inorganiques comprenant des spheres fines de dimension uniforme

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(56) References cited:
EP-A- 0 363 926 EP-A- 0 363 927
JP-A-63 244 988 US-A- 3 352 950

• DATABASE WPIL, accession no. 76-69402X [37],
Derwent Publications Ltd, London, GB & JP-A-
51086075 (Agency of Ind. Sci: Tech.)
• DATABASE WPIL, accession no. 78-27830A [15],
Derwent Publications Ltd, London, GB; & JP-A-
53 022 530 (AGENCY OF IND. SCI. TECH.)

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Description

Background of the Invention

1. Field of the Invention

The present invention relates to a process for producing an inorganic particulate material in the form of fine balls of uniform size, and more particularly to a process for producing such inorganic particulate material utilizing a solution reaction.

The inorganic particulate material obtained by the process of the invention comprises porous or nonporous fine balls which are uniform in size. Since the present material is substantially uniform in particle size, it is usable as a sustained-release inorganic microcapsule film material for enclosing perfumes, dyes, disinfectants, insecticides, repellents for insects and animals, vitamins, foods, nutrients, medicinals, deodorants, adhesives, liquid crystals, etc. in a wide variety of applications.

The present material is useful also as an extender pigment, for example, in the fields of cosmetics, coating compositions, plastics, inks, and agents for preventing adhesion of films.

Moreover, pigments, dyes or like coloring substances can be enclosed with the present material to form colored fine balls of uniform size, so that the material produces excellent effects when used as an additive for cosmetics, inks and plastics.

The material is expected to exhibit outstanding properties for use as a filler for high-performance chromatographs and gas chromatographs, magnetic tape and catalyst, and is also usable for spacers for liquid crystals.

2. Description of the Prior Art

Processes are already known for preparing inorganic particulate materials comprising porous fine balls with use of solutions, as disclosed, for example, in Examined Japanese Patent Applications JP-A-51086075 and JP-A-53022530.

These conventional processes consist essentially of mixing together an aqueous solution of water-soluble inorganic compound and an organic solvent to prepare a W/O emulsion, and subsequently mixing the emulsion with an aqueous solution capable of forming a water-insoluble precipitate when reacted with the water-soluble inorganic compound to produce porous fine balls of inorganic material.

Although the process described is an excellent process for producing an inorganic particulate material in the form of fine porous balls, the process has the tendency for the particles obtained to vary in size and encounters difficulty in preparing fine balls of substantially uniform size.

On the other hand, various processes are known for preparing emulsions. Recently developed is a process for producing an emulsion using a micro porous mem-

brane as disclosed in Japanese Patent Application JP-A-63244988.

With this process, a liquid serving as the dispersed phase is forced into a liquid for providing the continuous phase through the micro porous membrane having pores of uniform diameter to obtain an emulsion.

We have conducted research on processes wherein the solution reaction is utilized for preparing porous inorganic particulate materials in order to overcome the above drawback.

During the research, we conceived the entirely novel idea that the emulsion producing technique using the micro porous membrane would be applicable to the preparation of such an inorganic particulate material. We have carried out further research based on this novel idea.

Summary of the Invention

Accordingly, the main object of the present invention is to overcome the foregoing drawback of the prior art, that is, to develop a process for producing an inorganic particulate material comprising fine balls of approximately uniform size using a micro porous membrane.

The above object is fulfilled by a process, for producing an inorganic particulate material in the form of fine balls, which comprises the steps of:

a) providing a first aqueous solution comprising water and at least one compound (I) of the group consisting of halides of alkaline earth metals, inorganic acids, organic acids, ammonium salts of inorganic acids, ammonium salts of organic acids, and carbonates of alkali metals;

b) providing a second aqueous solution comprising water and at least one compound (II) of the group consisting of silicates, carbonates, phosphates or sulfates of alkali metals, halides of alkaline earth metals, and sulfates, hydrochlorides or nitrates of copper family elements or iron family elements, wherein the compound of the second aqueous solution forms a water-insoluble precipitate when reacted with the compound of the first aqueous solution;

c) forming a water-in-oil emulsion by passing the second aqueous solution into at least one organic solvent (III) through a microporous membrane having micropores of uniform diameter and rendered hydrophobic; and

d) mixing the first aqueous solution with the water-in-oil emulsion, whereby the uniform size inorganic balls are formed.

Alternatively, the process may comprise the steps of:

a) providing a first aqueous solution comprising water and at least one compound (i) of the group consisting of halides of alkaline earth metals, inorganic acids, organic acids, ammonium salts of inorganic acids, ammonium salts of organic acids, and carbonates of alkali metals ;

b) providing a second aqueous solution comprising water and at least one compound (ii) of the group consisting of silicates, carbonates, phosphates or sulfates of alkali metals, halides of alkaline earth metals, and sulfates, hydrochlorides or nitrates of copper family elements or iron family elements, wherein the compound of the second aqueous solution forms a water-insoluble precipitate when reacted with the compound of the first aqueous solution ;

c) mixing the first aqueous solution with the second aqueous solution to form an aqueous solution of unreacted material ;

d) forming a water-in-oil emulsion by passing the aqueous solution of unreacted material into at least one organic solvent (iii) through a microporous membrane having micropores of uniform diameter and rendered hydrophobic ;

e) reacting the water-in-oil emulsion, whereby the uniform size inorganic balls are formed.

Our research has revealed that when the micro porous membrane having micropores of uniform diameter and to be used for forcing the aqueous solution of inorganic compound (ii) into the organic solvent (iii) is a membrane subjected to a treatment for making the membrane hydrophobic, the aqueous solution can be forced into the organic solvent to provide an emulsion which is uniform in particle size, consequently giving the desired product comprising fine balls of approximately uniform size.

The present invention has been accomplished based on this novel discovery.

The said above object is also fulfilled by the process according to claim 2.

Brief Description of the Drawings

FIG. 1 is a diagram schematically showing an apparatus for use in practicing the process of the invention;

FIGS. 2 and 4 are scanning electron photomicrographs showing particulate materials of the invention;

FIGS. 3 and 5 are particle size distribution diagrams of the materials of FIGS. 2 and 4, respectively;

FIGS. 6 and 8 are scanning electron photomicrographs showing particulate materials prepared by processes other than the process of the invention; and

FIGS. 7 and 9 are particle size distribution diagrams of the materials of FIGS. 6 and 8, respectively.

Description of the Preferred Embodiments

The essential features of the present invention are:

(a) To basically use a conventional process wherein the solution reaction is utilized for producing an inorganic particulate material comprising porous fine balls.

(b) To use a micro porous membrane having micropores of uniform diameter as means for preparing a W/O emulsion in the process.

(c) To use the micro porous membrane after it has been rendered hydrophobic by a pre-treatment.

According to the present invention wherein a W/O emulsion is prepared, use of a mere micro porous membrane fails to afford such an emulsion wherein the suspended particles are minute and uniform in size, whereas the micro porous membrane, when used as rendered hydrophobic, provides a W/O emulsion comprising minute particles of substantially uniform size.

This is an entirely novel finding we have obtained.

The above features will be described in the order mentioned.

The conventional process (a), which can be practiced as it is, is for example the one disclosed in Japanese Patent Applications JP-A-51086075 or JP-A-53022530.

Stated more specifically, an aqueous solution is prepared which contains at least one inorganic compound at a concentration of 0.3 mole/liter to saturation, the compound being selected from among silicates, carbonates, phosphates or sulfates of alkali metals, halides of alkaline earth metals, and sulfates, hydrochlorides or nitrates of copper family elements or iron family elements.

Next, an organic solvent having a solubility in water preferably of up to 5% is admixed with the aqueous solution to prepare a W/O emulsion.

Of course, a micro porous membrane made hydrophobic is according to the invention used in this step.

Subsequently, an aqueous solution of at least one compound selected from among halides of alkaline earth metals, inorganic acids, organic acids, ammonium salts of inorganic acids, ammonium salts of organic acids and carbonates of alkali metals and capable of forming a water-insoluble precipitate when subjected to an aqueous solution reaction with the inorganic compound is prepared which has a concentration of 0.05 mole/liter to saturation, preferably 0.1 to 2.0 moles/liter. This aqueous solution is admixed with the W/O emulsion in an amount of 100 parts by weight per 100 parts by weight of the emulsion.

Consequently, an inorganic particulate material is obtained which comprises fine balls of uniform size.

The uniformity of particle sizes of the inorganic particulate material was evaluated in terms of the dispersion ϵ of particle sizes represented by the following equation:

$$\epsilon = (D_{90} - D_{10})/D_{50}$$

wherein D10, D50 and D90 are particle sizes corresponding to cumulative amounts of 10%, 50% and 90% on a cumulative particle size curve obtained by determining the distribution of sizes of the particles formed by centrifugal sedimentation absorptiometry.

$\epsilon = 0$ means no dispersion. The greater the value ϵ , the greater is the dispersion.

According to the present invention, the particulate material is evaluated as being approximately uniform in particle size when ϵ is smaller than about 1.3. If the value is greater, the particles are interpreted as being of varying sizes.

Examples of preferred organic solvents which are up to 5% in solubility in water are as follows.

Aliphatic hydrocarbons:

n-Hexane, isohexane, n-heptane, isooheptane, n-octene, iso-octene, gasoline, petroleum ether, kerosene, benzene, mineral spirit and the like.

Alicyclic hydrocarbons:

Cyclopentane, cyclohexane, cyclohexene, cyclononane and the like.

Aromatic hydrocarbons:

Benzene, toluene, xylene, ethylbenzene, propylbenzene, cumene, mesitylene, tetralin, styrene and the like.

Ethers:

Propyl ether, isopropyl ether and the like.

Hydrocarbon halides:

Methylene chloride, chloroform, ethylene chloride, trichloroethane, trichloroethylene and the like.

Esters:

Ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, n-amyl acetate, isoamyl acetate, butyl lactate, methyl propionate, ethyl propionate, butyl propionate, methyl butyrate, ethyl butyrate, butyl butyrate and the like.

These organic solvents are usable singly, or at least two of them can be used in admixture.

The W/O emulsion to be prepared has a W/O ratio of 4/1 to 1/5, preferably about 2/1 to about 1/2. Surfactants are used in an amount of up to about 10 wt.%, preferably about 0.1 to about 3 wt.%, of the organic solvent.

Nonionic surfactants are used. Examples of preferred surfactants are as follows.

Polyoxyethylene sorbitan fatty acid esters:

Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan tristearate, polyoxyethylene sorbitan monooleate, polyoxyethylene sorbitan stearate and the like.

Polyoxyethylene higher alcohol ethers:

Polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl phenol ether, polyoxyethylene nonyl phenol ether and the like.

Polyoxyethylene fatty acid esters:

Polyoxyethylene glycol monolaurate, polyoxyethylene glycol monostearate, polyoxyethylene glycol stea-

rate, polyoxyethylene glycol monooleate and the like.

Glycerin fatty acid esters:

Stearic acid monoglyceride, oleic acid monoglyceride and the like.

Polyoxyethylene sorbitol fatty acid esters:

Tetraoleic acid polyoxyethylene sorbitol and the like.

Among these surfactants, polyoxyethylene sorbitan fatty acid esters are especially preferable. These surfactants are used singly, or at least two of them are used in admixture.

According to the present invention, the basic process includes various conventional methods of causing the fine balls of inorganic particulate material to support pigments, coloring substances, perfumes, microorganisms or the like.

Further according to the present invention, the basic process (a) includes the process disclosed in Unexamined Japanese Patent Publication SHO 63-25864 for producing a hollow inorganic particulate material.

This process comprises admixing an organic solvent with an aqueous solution containing at least one inorganic compound selected from among silicates, carbonates, phosphates or sulfates of alkali metals, halides of alkaline earth metals, and sulfates, hydrochlorides or nitrates of copper family elements or iron family elements to prepare a W/O emulsion, and subsequently admixing with the emulsion an aqueous solution of a compound selected from among halides of alkaline earth metals, inorganic acids, organic acids, ammonium salts of inorganic acids, ammonium salts of organic acids and carbonates of alkali metals and capable of forming a water-insoluble precipitate when subjected to an aqueous solution reaction with the inorganic compound to prepare an inorganic particulate material comprising fine balls of approximately uniform size, the process being characterized by:

- (A) admixing an organic solvent containing a hydrophilic surfactant with the aqueous solution of inorganic compound to prepare an O/W emulsion,
- (B) admixing the O/W emulsion obtained with an organic solvent containing a hydrophilic surfactant to obtain an O/W/O emulsion, and
- (C) subsequently admixing the O/W/O emulsion obtained by the step (B) with the aqueous solution of the compound capable of forming a water-insoluble precipitate by the aqueous solution reaction, whereby

a hollow inorganic particulate material of fine balls is produced. A micro porous membrane is used for preparing at least the emulsion in the step (B), preferably for preparing both the emulsions in the steps (A) and (B).

The micro porous membrane to be used for preparing the W/O emulsion in the above process must be one subjected to a treatment for making the membrane hydrophobic. The O/W emulsion is prepared using a micro porous membrane not rendered hydrophobic.

Next, the features (b) and (c) of the invention will be described.

Useful as the means of the feature (b) are basically the method disclosed in Japanese Patent Application JP-A-63244988 and the micro porous membrane used in this method.

However, the micro porous membrane for use in the present invention is rendered hydrophobic before use. Useful micro porous membranes are those having micropores which are uniform in diameter. The pore diameter is suitably determined in accordance with the particle size of the desired product, i.e., fine balls.

Stated more specifically, desirable micro porous membranes for use in the invention are as follows.

- (1) Membranes having micropores extending there-through, uniform in diameter and as small as possible in the distribution of pore diameters.
- (2) Membranes having micropores which are adjustable to the desired diameter (usually about 0.1 to about 10 μ m).
- (3) Membranes having a sufficient mechanical strength against deformation or breaking when the liquid to be made into the dispersed phase is forced into the liquid serving as the continuous phase.
- (4) Membranes having chemical resistance to the liquids for forming the emulsion.

Micro porous membranes having such characteristics are those made of inorganic material or organic material and are not limited specifically. Examples of useful membranes are those made of the CaO-B₂O₃-SiO₂-Al₂O₃ porous glass disclosed in Examined Japanese Patent Publication SHO 62-25618, those made of the CaO-B₂O₃-SiO₂-Al₂O₃-Na₂O porous glass and CaO-B₂O₃-SiO₂-Al₂O₃-Na₂O-MgO porous glass disclosed in Unexamined Japanese Patent Publication SHO 61-40841 (US-A-4,657,875), etc. These porous glasses have the feature that the pores are controlled to a very narrow range of diameters and are circular in cross section. Although the membrane is not limited specifically in thickness, the thickness is preferably about 0.4 to about 2mm in view of strength, etc.

The method of making the micro porous membrane hydrophobic is not limited specifically insofar as the membrane is rendered so hydrophobic that the W/O emulsion can be prepared with use of the membrane.

To make the micro porous membrane hydrophobic, a hydrophobicity imparting agent is applied to the entire surface of the membrane and caused to be chemically absorbed by the membrane or to physically form a hydrophobic film over the membrane. Different kinds of such agents are usable in combination. The membrane is made hydrophobic to the desired extent insofar as the agent will not close the micropores and will not separate off the membrane during the preparation of the W/O emulsion.

Examples of preferred hydrophobicity imparting agents are dimethylpolysiloxane, methylhydrogenpolysil-

oxane and like thermosetting silicone oils, silicone emulsion, silicone resin and like resins, methyltrimethoxysilane, hexamethyldisilane, vinyltrimethoxysilane, trimethylchlorosilane and like silane coupling agents, dihydrogenhexamethylcyclotetrasiloxane, trihydrogenpentamethylcyclotetrasiloxane and like cyclic silicone compounds, isopropyltristearoyl titanate, isopropyltri (N-aminoethyl) titanate and like titanate coupling agents, acetoalkoxyaluminum diisopropylate and like aluminum coupling agents, fluorosilicone coating agent, fluorine-containing coating agent, etc. Some of these agents are usable in combination.

Although extreme difficulties have heretofore been encountered in preparing inorganic particulate materials comprising fine balls of approximately uniform size, such materials can be produced by the process of the invention utilizing a solution reaction.

Examples

The present invention will be described in greater detail with reference to the following examples.

Example 1:

A hollow cylindrical micro porous membrane of glass, 1.05 μ m in micropore diameter, was dried at 110°C for 24 hours and thereafter dipped in a 10 wt.% toluene solution of trimethylchlorosilane at room temperature for treatment with the silane coupling agent and thereby made hydrophobic.

The hydrophobic micro porous membrane was installed in the apparatus shown in FIG.1. Using the apparatus, water glass No.3 (4 moles/liter calculated as SiO₂) was forced through the membrane into 800ml of hexane solution of 20g/liter of polyoxyethylene (20) sorbitan trioleate as a continuous phase for 1 hour under a nitrogen gas pressure of 39226 Pa (0.4kgf/cm²) to prepare a W/O emulsion. The reference numerals given in FIG. 1 represent the following components.

- 1: Cylindrical micro porous glass membrane
- 2: Module
- 3: Pump
- 4: Pressure gauge
- 5: O-phase (oil phase) line
- 6: W-phase (water phase) line
- 8: O-phase (oil phase) line
- 7: W-phase (water phase) line
- 9: Pressurizing gas cylinder
- 10: Pressure gauge

The emulsion was added to and reacted with 1 liter of ammonium bicarbonate solution having a concentration of 1.5 moles/liter and prepared in advance, followed by standing for 2 hours and filtration. The cake filtered off was washed with water and then with methanol and thereafter dried at 110°C for 24 hours.

The above procedure gave a porous particulate silica in the form of fine balls which were approximately uniform in size and $3.47\mu\text{m}$ in mean size.

FIG. 2 is a scanning electron photomicrograph of the particulate silica (X1000), and FIG. 3 shows the particle size distribution of the silica.

$D_{10} = 2.25$, $D_{50} = 3.47$, $D_{90} = 4.99$

Dispersion $\varepsilon = (4.99 - 2.25) / 2.76 = 0.79$

Example 2:

A hollow cylindrical micro porous glass membrane, $0.28\mu\text{m}$ in micropore diameter, was dried at 110°C for 24 hours, thereafter dipped in a 10 wt.% toluene solution of silicone resin (SR-2410, product of Toray Dow Corning Silicone Co., Ltd.) at room temperature, dried at 110°C for 24 hours and thus coated with the silicone resin, whereby the membrane was made hydrophobic.

In the same manner as in Example 1, the hydrophobic micro porous membrane was installed in the apparatus of FIG. 1, and using the apparatus, water glass No. 3 (4 moles/liter calculated as SiO_2) was forced through the membrane into 800ml of toluene solution of 15g/liter of sorbitan monolaurate as a continuous phase for 1 hour under a nitrogen gas pressure of 196133 Pa (2.0kgf/cm^2) to prepare a W/O emulsion.

The emulsion was added to and reacted with 1 liter of ammonium sulfate solution having a concentration of 3.0 moles/liter and prepared in advance, followed by standing for 2 hours and filtration. The cake separated off was washed with water and then with methanol and thereafter dried at 110°C for 24 hours, consequently affording a porous particulate silica in the form of fine balls which were approximately uniform in size and $1.21\mu\text{m}$ in mean size.

FIG. 4 is a scanning electron photomicrograph of the particulate silica, and FIG. 5 shows the particle size distribution of the silica.

$D_{10} = 0.64$, $D_{50} = 1.21$, $D_{90} = 2.05$

Dispersion $\varepsilon = (2.05 - 0.64) / 1.21 = 1.17$

Example 3:

A hollow cylindrical micro porous glass membrane, $1.10\mu\text{m}$ in micropore diameter, was dried at 110°C for 24 hours, thereafter dipped in a fluorosilicone coating agent (KP-801M, product of Shin-Etsu Chemical Co., Ltd.) at room temperature, dried at 110°C for 24 hours and thus formed with a fluorosilicone coating, whereby the membrane was made hydrophobic.

To 500ml of water glass No. 3 (6.5 moles/liter calculated as SiO_2) was added 100ml of kerosene solution of 10g/liter of polyoxyethylene ($n=10$) nonyl phenyl ether, and the mixture was stirred at a high speed by a homogenizer to prepare an O/W emulsion.

In the same manner as in Example 1, the hydrophobic micro porous membrane was installed in the apparatus of FIG. 1, and using the apparatus, the emulsion was forced through the membrane into 800ml of toluene

solution of 15g/liter of sorbitan monolaurate as a continuous phase for 1 hour under a nitrogen gas pressure of 78453 Pa (0.8kgf/cm^2) to prepare a O/W/O emulsion.

The emulsion was added to and reacted with 2 liters of potassium chloride solution having a concentration of 1.5 moles/liter and prepared in advance. The reaction mixture was allowed to stand for 6 hours and filtered. The cake separated off was washed with water and then with methanol and thereafter dried at 110°C for 24 hours, consequently affording a particulate calcium silicate in the form of hollow porous fine balls which were approximately uniform in size and $3.50\mu\text{m}$ in mean size.

Example 4:

A hollow cylindrical micro porous glass membrane, $1.10\mu\text{m}$ in micropore diameter, was dried at 110°C for 24 hours, thereafter dipped in a 10 wt.% aqueous solution of water-soluble organosilicon resin (KP-18C, product of Shin-Etsu Chemical Co., Ltd.) at room temperature, dried at 110°C for 24 hours and thus coated with the silicone resin, whereby the membrane was made hydrophobic.

In the same manner as in Example 1, the hydrophobic micro porous membrane was installed in the apparatus of FIG. 1, and using the apparatus, an aqueous solution of 2.5 moles/liter of nickel sulfate was forced through the membrane into 800ml of toluene solution of 15g/liter of sorbitan monooleate as a continuous phase for 1 hour under a nitrogen gas pressure of 37265.3 Pa (0.38kgf/cm^2) to prepare a W/O emulsion.

The emulsion was added to and reacted with 500ml of potassium hydrogencarbonate aqueous solution having a concentration of 3.0 moles/liter and prepared in advance, followed by standing for 2 hours and filtration. The cake separated off was washed with water and then with methanol and thereafter dried at 110°C for 24 hours, consequently giving a basic particulate nickel carbonate in the form of porous balls which were approximately uniform in size and $2.86\mu\text{m}$ in mean size.

The product was further heated in air at 500°C for 24 hours to obtain a particulate nickel oxide in the form of porous fine balls which were approximately uniform in size.

Example 5:

A hollow cylindrical micro porous glass membrane, $2.00\mu\text{m}$ in micropore diameter, was dried at 110°C for 24 hours, thereafter dipped in a 5 wt.% hexane solution of silicone resin (SR-2405, product of Toray Dow Corning Silicone Co., Ltd.) at room temperature, dried at 110°C for 24 hours and thus coated with the silicone resin, whereby the membrane was made hydrophobic.

In the same manner as in Example 1, the hydrophobic micro porous membrane was installed in the apparatus of FIG. 1. A 200ml quantity of commercial water glass No. 3 (4 moles/liter calculated as SiO_2) was dissolved in 300ml of ion-exchanged water, and the water

glass solution was maintained at a temperature of up to 20°C and admixed in small portions with 400ml of dilute sulfuric acid with ice cooling. Using the apparatus and with ice cooling, the mixture was forced through the membrane into 1000ml of toluene solution of 15g/liter of sorbitan monolaurate as a continuous phase for 30 minutes under a nitrogen gas pressure of 19613.3 Pa (0.2kgf/cm²) to prepare a W/O emulsion.

The emulsion was maintained at room temperature for 10 minutes with stirring, then gradually heated to about 50°C with continued stirring and thereafter allowed to gel over a period of about 5 hours.

The gel was filtered, and the cake separated off was washed with water and then with methanol and dried at 110°C for 24 hours, affording a particulate silica gel comprising porous balls which were approximately uniform in size and 6.02µm in mean size.

Example 6:

A hollow cylindrical micro porous glass membrane, 10.00µm in micropore diameter, was dried at 110°C for 24 hours, thereafter dipped in a 10 wt.% aqueous solution of water-soluble organosilicon resin (KP-18C, product of Shin-Etsu Chemical Co., Ltd.) at room temperature, dried at 110°C for 24 hours and thus coated with the silicone resin, whereby the membrane was made hydrophobic.

In the same manner as in Example 1, the hydrophobic micro porous membrane was installed in the apparatus of FIG. 1, and using the apparatus, a dispersion of 60g of titanium oxide (JR-801, product of Teikoku Kako Co., Ltd.) in 500ml of water glass No. 3 (4 moles/liter calculated as SiO₂) prepared by a homo disper was forced through the membrane into 800ml of kerosene solution of 15g/liter of sorbitan monooleate as a continuous phase for 20 minutes under a nitrogen gas pressure of 9806.6 Pa (0.1kgf/cm²) to prepare a W/O emulsion.

The emulsion was added to and reacted with 1 liter of ammonium bicarbonate solution having a concentration of 1.5 moles/liter and prepared in advance, followed by standing for 2 hours and filtration. The cake separated off was washed with water and then with methanol and thereafter dried at 110°C for 24 hours, consequently giving colored spherical fine silica particles having 25% of titanium oxide enclosed therein, approximately uniform in size and 21.4µm in mean size.

Reference Example 1:

According to a conventional process wherein solutions are utilized for preparing an inorganic particulate material comprising porous fine balls, e.g., according to the process disclosed in Japanese Patent Applications JP-A-51086075 or JP-A-53022530, 200ml of water glass No. 3 (4 moles/liter calculated as SiO₂) was added to 600ml of hexane solution of 20g/liter of polyoxyethylene (20) sorbitan trioleate placed in a 1 liter beaker and serving as a continuous phase, followed by stirring at a

high speed of 8000r.p.m. for 1 minute by a homogenizer to prepare a W/O emulsion.

The emulsion was added to and reacted with 1 liter of ammonium bicarbonate solution having a concentration of 1.5 moles/liter and prepared in advance, followed by standing for 2 hours and filtration. The cake separated off was washed with water and then with methanol and dried at 110°C for 24 hours.

The above procedure gave a particulate silica in the form of porous fine balls which were not uniform in size and 3.35µm in mean particle size.

FIG. 6 is a scanning electron photomicrograph of the silica, and FIG. 7 shows the particle size distribution thereof.

D10 = 2.01, D50 = 3.35, D90 = 9.23

Dispersion $\epsilon = (9.23-2.01)/3.35 = 2.16$

Reference Example 2:

A hollow cylindrical micro porous glass membrane, 1.05µm in micropore diameter, was dried at 110°C for 24 hours and thereafter installed in the apparatus of FIG. 1 as in Example 1 without rendering the membrane hydrophobic in any way. Using the apparatus, water glass No. 3 (4 moles/liter calculated as SiO₂) was forced through the membrane into 800ml of hexane solution of 20g/liter of polyoxyethylene (20) sorbitan trioleate as a continuous phase for 20 minutes under a nitrogen gas pressure of 9806.6 Pa (0.1kgf/cm²) to prepare a W/O emulsion.

The emulsion was added to and reacted with 1 liter of ammonium bicarbonate solution having a concentration of 1.5 moles/liter and prepared in advance. The reaction mixture was allowed to stand for 2 hours and filtered. The cake separated off was washed with water and then with methanol and thereafter dried at 110°C for 24 hours.

The above procedure afforded a particulate silica comprising porous fine balls greatly varying in size and having mean particle size of 5.35µm.

FIG. 8 is a scanning electron photomicrograph of the silica, and FIG. 9 shows the particle size distribution thereof.

D10 = 2.83, D50 = 5.35, D90 = 10.35

Dispersion $\epsilon = (10.35-2.83)/5.35 = 1.41$

Claims

1. A process for producing inorganic particulate material in the form of fine balls approximately uniform in size characterized in that it comprises the steps of :

- a) providing a first aqueous solution comprising water and at least one compound of the group consisting of halides of alkaline earth metals, inorganic acids, organic acids, ammonium salts of inorganic acids, ammonium salts of organic acids, and carbonates of alkali metals ;
- b) providing a second aqueous solution comprising water and at least one compound of the group consisting of silicates, carbonates, phos-

phates or sulfates of alkali metals, halides of alkaline earth metals, and sulfates, hydrochlorides or nitrates of copper family elements or iron family elements, wherein the compound of the second aqueous solution forms a water-insoluble precipitate when reacted with the compound of the first aqueous solution ;

c) forming a water-in-oil emulsion by passing the second aqueous solution into at least one organic solvent through a microporous membrane having micropores of uniform diameter and rendered hydrophobic ; and

d) mixing the first aqueous solution with the water-in-oil emulsion, whereby the uniform size inorganic balls are formed.

2. A process for producing inorganic particulate material in the form of fine balls approximately uniform in size characterized in that it comprises the steps of :

a) providing a first aqueous solution comprising water and at least one compound of the group consisting of halides of alkaline earth metals, inorganic acids, organic acids, ammonium salts of inorganic acids, ammonium salts of organic acids, and carbonates of alkali metals ;

b) providing a second aqueous solution comprising water and at least one compound of the group consisting of silicates, carbonates, phosphates or sulfates of alkali metals, halides of alkaline earth metals, and sulfates, hydrochlorides or nitrates of copper family elements or iron family elements, wherein the compound of the second aqueous solution forms a water-insoluble precipitate when reacted with the compound of the first aqueous solution ;

c) mixing the first aqueous solution with the second aqueous solution to form an aqueous solution of unreacted material ;

d) forming a water-in-oil emulsion by passing the aqueous solution of unreacted material into at least one organic solvent through a microporous membrane having micropores of uniform diameter and rendered hydrophobic ;

e) reacting the water-in-oil emulsion, whereby the uniform size inorganic balls are formed.

Patentansprüche

1. Verfahren zur Erzeugung anorganischen Teilchenmaterials in der Form feiner Kugeln angenähert gleichmäßiger Größe, dadurch gekennzeichnet, daß es die Schritte aufweist:

a) Vorsehen einer ersten wässrigen Lösung, die Wasser und wenigstens eine Verbindung der Gruppe enthält, die aus Erdalkalimetallhalogeniden, anorganischen Säuren, organischen

Säuren, Ammoniumsalzen anorganischer Säuren, Ammoniumsalzen organischer Säuren und Alkalimetallkarbonaten besteht;

b) Vorsehen einer zweiten wässrigen Lösung, die Wasser und wenigstens eine Verbindung der Gruppe enthält, die aus Alkalimetallsilikaten, -karbonaten, -phosphaten oder -sulfaten, Erdalkalimetallhalogeniden und Sulfaten, Hydrochloriden oder Nitraten der Kupferfamilienelemente oder Eisenfamilienelemente besteht, wobei die Verbindung der zweiten wässrigen Lösung bei Reaktion mit der Verbindung der ersten wässrigen Lösung eine wasserunlösliche Ausfällung bildet;

c) Bilden einer Wasser-in-Öl-Emulsion mittels Leitens der zweiten wässrigen Lösung durch eine Mikroporen gleichmäßigen Durchmessers aufweisende und hydrophob gemachte mikroporöse Membran in wenigstens ein organisches Lösungsmittel; und

d) Vermischen der ersten wässrigen Lösung mit der Wasser-in-Öl-Emulsion, wodurch die anorganischen Kugeln gleichmäßiger Größe gebildet werden.

2. Verfahren zur Erzeugung anorganischen Teilchenmaterials in der Form feiner Kugeln angenähert gleichmäßiger Größe, dadurch gekennzeichnet, daß es die Schritte aufweist:

a) Vorsehen einer ersten wässrigen Lösung, die Wasser und wenigstens eine Verbindung der Gruppe enthält, die aus Erdalkalimetallhalogeniden, anorganischen Säuren, organischen Säuren, Ammoniumsalzen anorganischer Säuren, Ammoniumsalzen organischer Säuren und Alkalimetallkarbonaten besteht;

b) Vorsehen einer zweiten wässrigen Lösung, die Wasser und wenigstens eine Verbindung der Gruppe enthält, die aus Alkalimetallsilikaten, -karbonaten, -phosphaten oder -sulfaten, Erdalkalimetallhalogeniden und Sulfaten, Hydrochloriden oder Nitraten der Kupferfamilienelemente oder Eisenfamilienelemente besteht, wobei die Verbindung der zweiten wässrigen Lösung bei Reaktion mit der Verbindung der ersten wässrigen Lösung eine wasserunlösliche Ausfällung bildet;

c) Vermischen der ersten wässrigen Lösung mit der zweiten wässrigen Lösung zum Bilden einer wässrigen Lösung unreaktierten Materials;

d) Bilden einer Wasser-in-Öl-Emulsion mittels Leitens der wässrigen Lösung unreaktierten Materials durch eine Mikroporen gleichmäßigen Durchmessers aufweisende und hydrophob gemachte mikroporöse Membran in wenigstens ein organisches Lösungsmittel; und

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c) Reaktion der Wasser-in-Öl-Emulsion, wodurch die anorganischen Kugeln gleichmäßiger Größe gebildet werden.

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Revendications

1. Procédé de production de matière particulaire inorganique sous forme de fines sphères de taille approximativement uniforme, caractérisé en ce qu'il comprend les étapes consistant à :

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a) fournir une première solution aqueuse comprenant de l'eau et au moins un composé du groupe constitué par les halogénures de métaux alcalino-terreux, les acides inorganiques, les acides organiques, les sels d'ammonium d'acides inorganiques, les sels d'ammonium d'acides organiques et les carbonates de métaux alcalins ;

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b) fournir une seconde solution aqueuse comprenant de l'eau et au moins un composé du groupe constitué par les silicates, les carbonates, les phosphates ou les sulfates de métaux alcalins, les halogénures de métaux alcalino-terreux et les sulfates, les chlorhydrates ou les nitrates d'éléments de la famille du cuivre ou d'éléments de la famille du fer, étant entendu que le composé de la seconde solution aqueuse forme un précipité insoluble dans l'eau lorsqu'il est mis à réagir avec le composé de la première solution aqueuse ;

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c) former une émulsion eau-dans-huile en faisant passer la seconde solution aqueuse dans au moins un solvant organique à travers une membrane microporeuse ayant des micropores de diamètre uniforme et que l'on a rendue hydrophobe et

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d) mélanger la première solution aqueuse avec l'émulsion eau-dans-huile, des sphères inorganiques de taille uniforme étant ainsi formées.

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2. Procédé de production de matière particulaire inorganique sous forme de fines sphères de taille approximativement uniforme, caractérisé en ce qu'il comprend les étapes consistant à :

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a) fournir une première solution aqueuse comprenant de l'eau et au moins un composé du groupe constitué par les halogénures de métaux alcalino-terreux, les acides inorganiques, les acides organiques, les sels d'ammonium d'acides inorganiques, les sels

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d'ammonium d'acides organiques et les carbonates de métaux alcalins ;

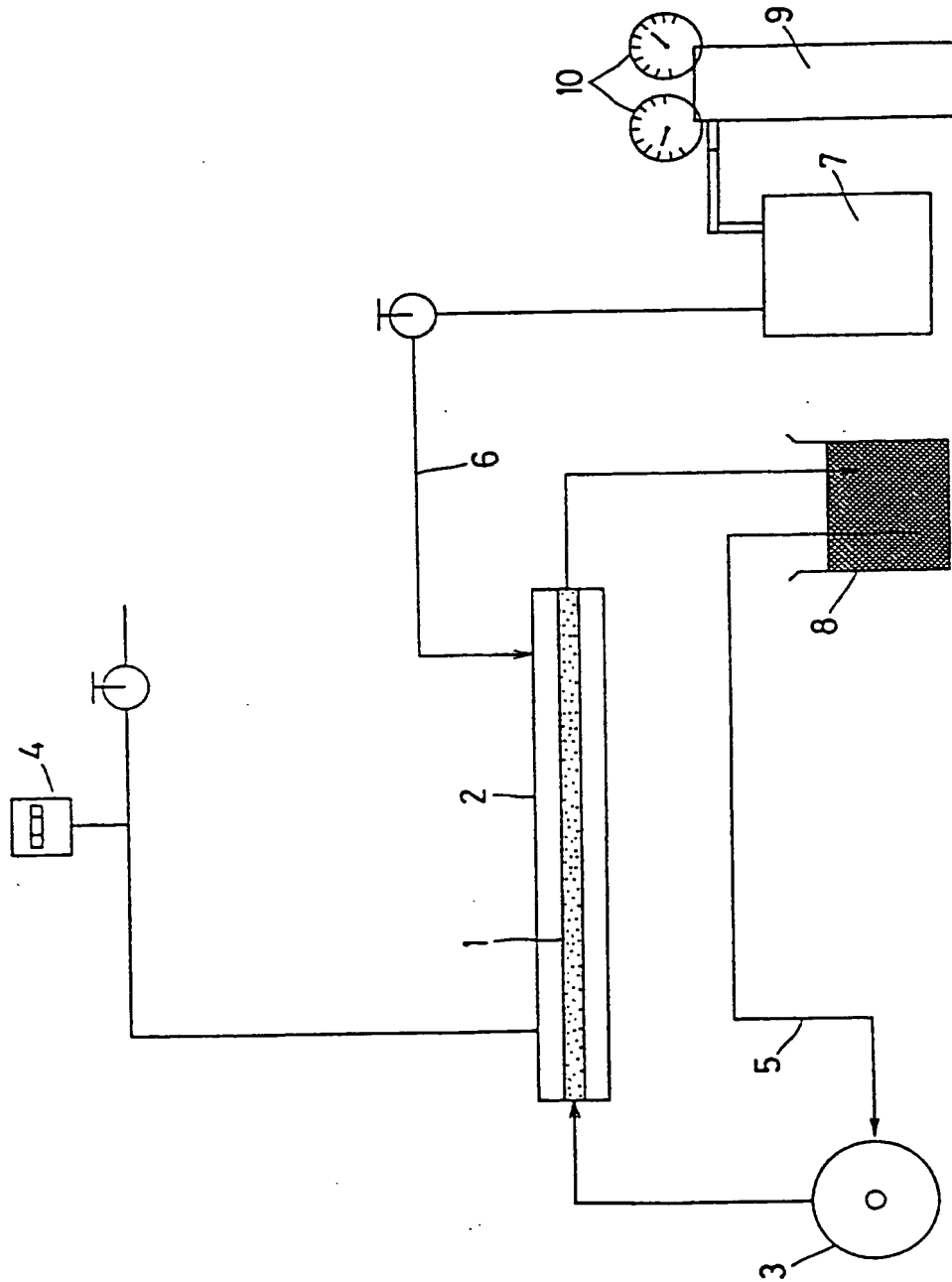
b) fournir une seconde solution aqueuse comprenant de l'eau et au moins un composé du groupe constitué par les silicates, les carbonates, les phosphates ou les sulfates de métaux alcalins, les halogénures de métaux alcalino-terreux et les sulfates, les chlorhydrates ou les nitrates d'éléments de la famille du cuivre ou d'éléments de la famille du fer, étant entendu que le composé de la seconde solution aqueuse forme un précipité insoluble dans l'eau lorsqu'il est mis à réagir avec le composé de la première solution aqueuse ;

c) mélanger la première solution aqueuse avec la seconde solution aqueuse pour former une solution aqueuse de matière n'ayant pas réagi ; d) former une émulsion eau-dans-huile en faisant passer la solution aqueuse de matière n'ayant pas réagi dans au moins un solvant organique à travers une membrane microporeuse ayant des micropores de diamètre uniforme et que l'on a rendue hydrophobe ;

e) mettre à réagir l'émulsion eau-dans-huile, les sphères inorganiques de taille uniforme étant ainsi formées.

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Fig.1



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Fig. 2

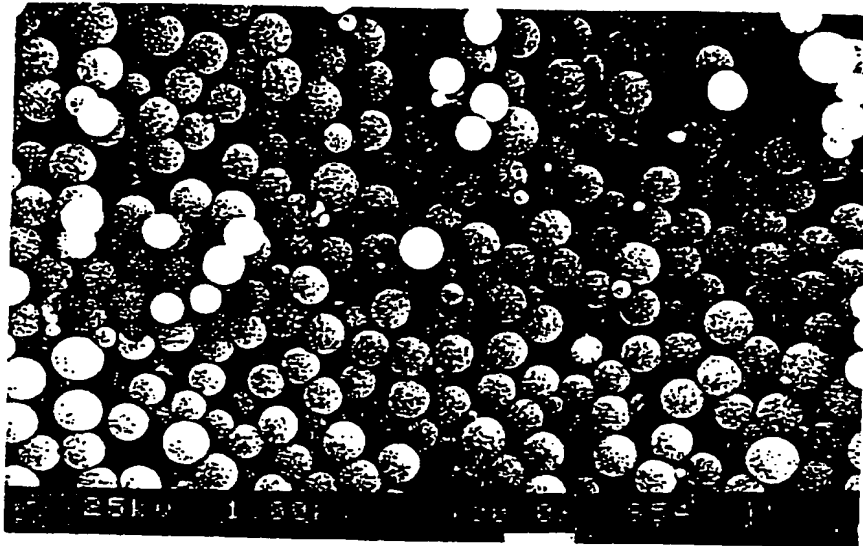
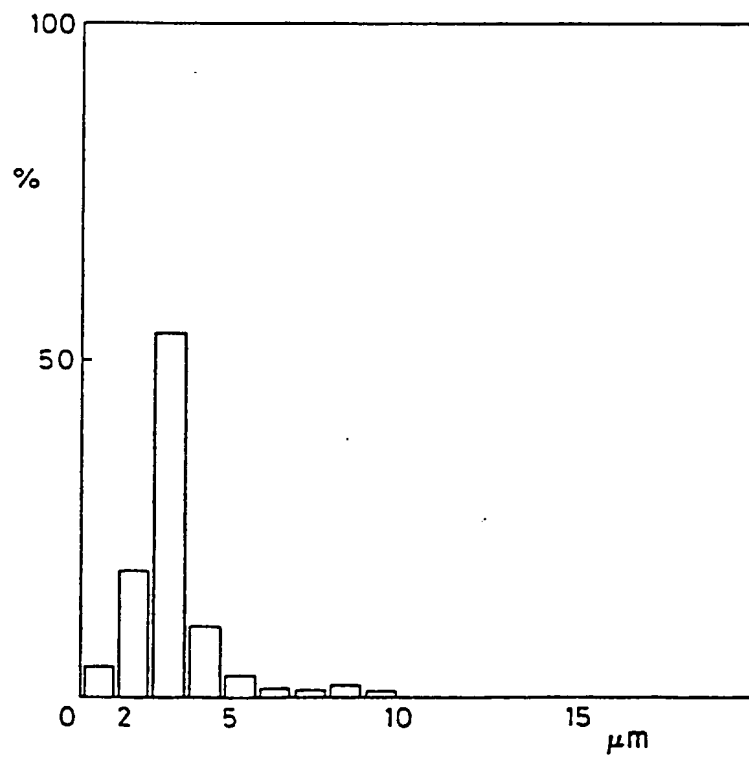


Fig. 3



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Fig.4

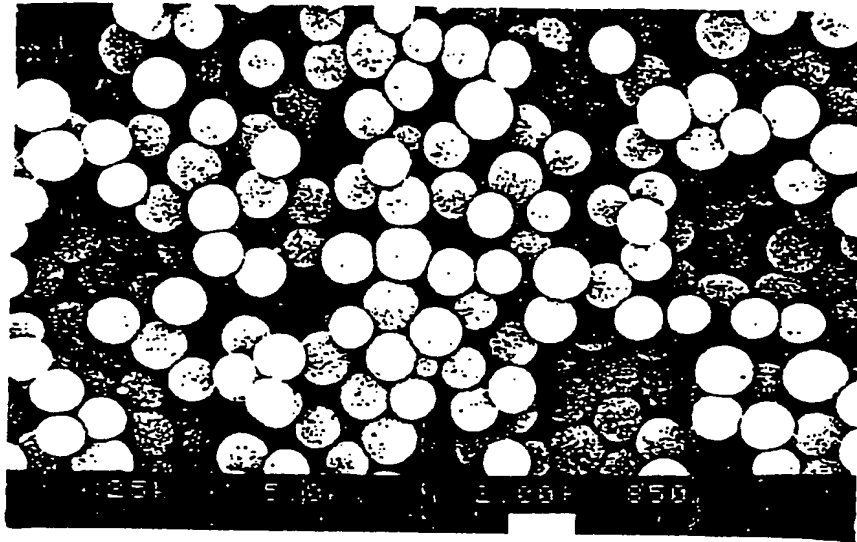
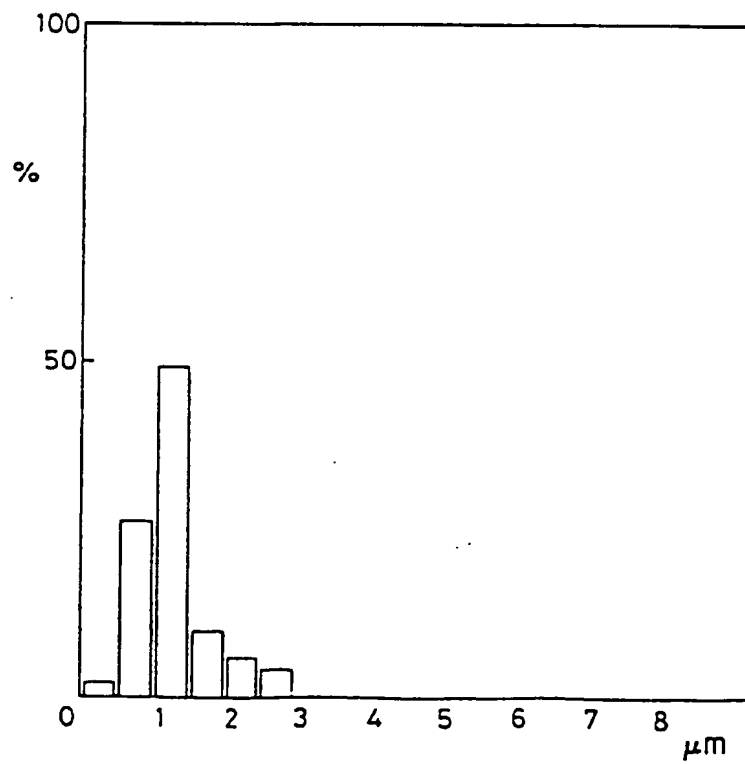


Fig.5



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Fig.6

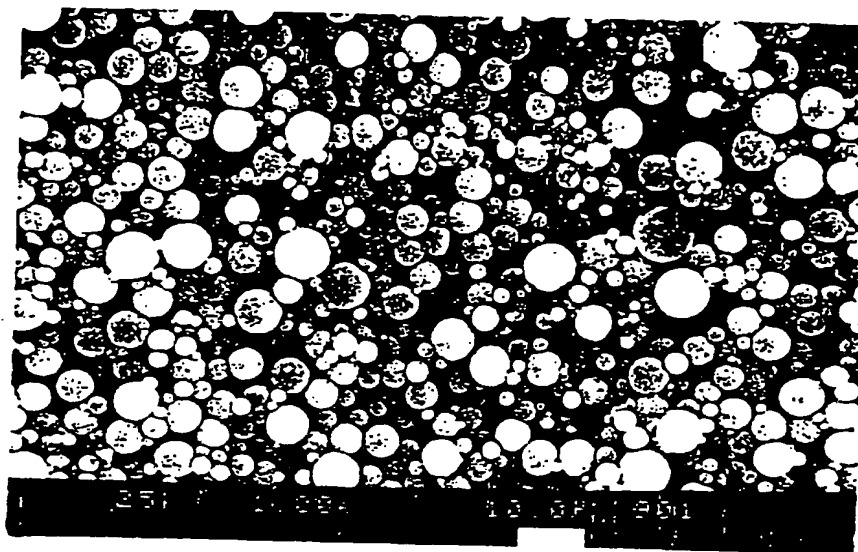
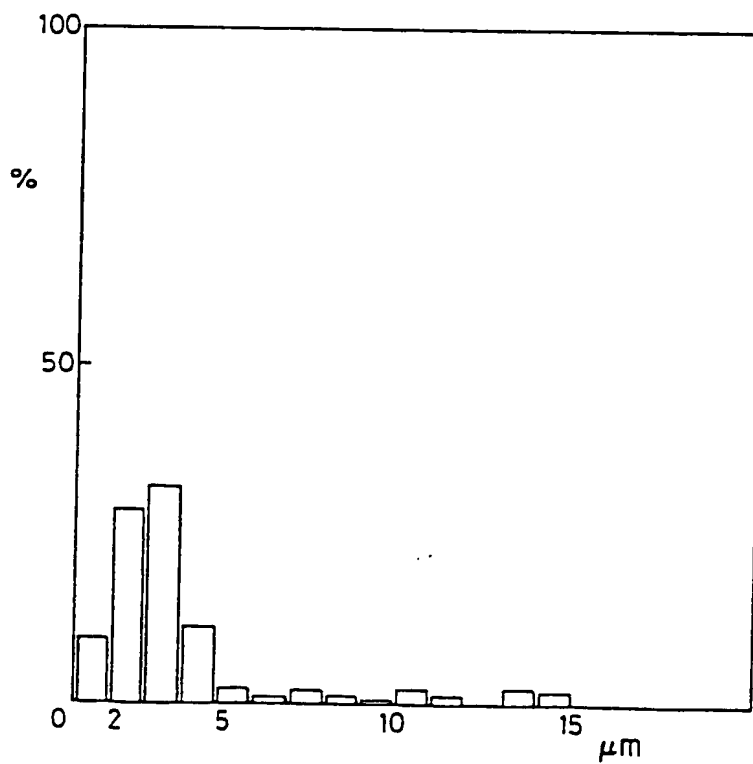


Fig.7



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Fig. 8

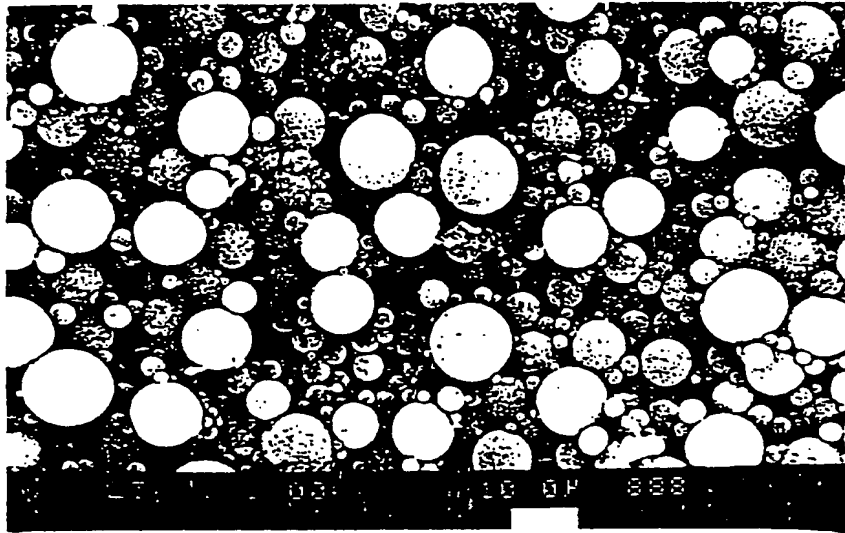


Fig. 9

